

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Lamotte et al.

Application No. Unassigned

Filed: June 26, 2001

For: MATERIAL AND METHOD FOR MAKING AN
ELECTROCONDUCTIVE PATTERN

Art Unit: Unassigned

Examiner: Unassigned

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CLAIM OF PRIORITY

Commissioner for Patents
Washington, D.C. 20231

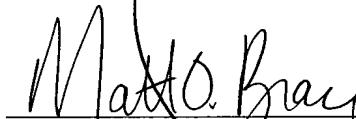
Dear Sir:

Applicants in the above-identified application, through the undersigned attorney, hereby request that the above-identified application be treated as entitled to the right accorded by Title 35, U.S. Code, Section 119, having regard to the application or the applications (if more than one application is set out below), which particulars are set out below:

European Application No. 00202216.8, filed June 26, 2000.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,



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Date: June 26, 2001

CERTIFICATE OF MAILING

I hereby certify that this CLAIM OF PRIORITY (along with any documents referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, Washington, D.C. 20231.

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Priority Claim (Rev. 03/21/2001)



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Bescheinigung

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Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00202216.8

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office
Le Président de l'Office européen des brevets
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I.L.C. HATTEN-HECKMAN

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Blatt 2 der Bescheinigung
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Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Material and method for making an electroconductive pattern

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[DESCRIPTION]

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(86)

FIELD OF THE INVENTION

5 The present invention relates to a method for making an electroconductive pattern in a conductive polymer layer.

BACKGROUND OF THE INVENTION

10 For the fabrication of flexible LC displays, electroluminescent devices and photovoltaic cells transparent ITO (Indium-Tinoxide) electrodes are used. These electrodes are made by vacuum sputtering of ITO onto a substrate. This method involves high temperatures, up to 250°C, and therefor glass substrates are generally used. Because 15 of the high fabrication costs, the low flexibility (pliability) and stretchability as a consequence of the brittleness of the ITO layer and the glass substrate, the range of potential applications is limited. Therefor the interest is growing in all-organic devices, comprising plastic resins as a substrate and organic 20 electroconductive polymer layers as electrode. Such plastic electronics allow to obtain low cost devices with new properties (Physics World, March 1999, p.25-39). Flexible plastic substrates can be provided with an electroconductive polymer layer by continuous roller coating methods (compared to batch process such as 25 sputtering) and the resulting organic electrodes enable the fabrication of electronic devices characterised by a higher flexibility and a lower weight.

30 The production and the use of electroconductive polymers such as polypyrrole, polyaniline, polyacetylene, polyparaphenylenes, polythiophene, polyphenylenevinylene, polythiophenevinylene and polyphenylenesulfide are known in the art. EP-A-440 957 describes a method for preparing polythiophene in an aqueous mixture by oxidative polymerisation in the presence of a polyanion as a doping agent. In EP-A-686 662 it has been disclosed that highly conductive 35 layers of polythiophene, coated from an aqueous coating solution, could be obtained by the addition of a di- or polyhydroxy and/or a carbonic acid, amide or lactam group containing compound in the coating solution of the polythiophene layer and by keeping the

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coated layer at elevated temperature, preferably between 100 and 250 °C, during preferably 1 to 90 seconds.

Coated layers of organic electroconductive polymers can be structured into patterns using known microlithography techniques.

5 In WO-A-97 18944 a process is described wherein a positive or negative photoresist is applied on top of a coated layer of an organic electroconductive polymer, and after the steps of selectively exposing the photoresist to UV light, developing the photoresist, etching the electroconductive polymer layer and finally 10 stripping the non-developed photoresist with an organic solvent, a patterned layer is obtained. A similar technique has been described in Synthetic Metals, 22 (1988), p. 265-271 for the design of an all-organic thin-film transistor. Such methods are cumbersome as they involve many steps and require the use of hazardous chemicals.

15

OBJECTS AND SUMMARY OF THE INVENTION

20 It is an object of the present invention to provide a material having an electroconductive polymer layer that can be patterned by a simple, convenient method which involves a low number of steps and which does not require the use of hazardous chemicals. These objects are realised by the materials having the specific features defined in claim 1 and 2. Preferred embodiments are defined in the dependent claims.

25

The materials of the present invention can be patterned by image-wise exposure followed by a single wet processing step. No etching liquids or organic solvents are required. Both embodiments defined in claims 1 and 2 are characterised by the common inventive feature that the electroconductive polymer and the light- or heat-sensitive layer can be simultaneously patterned by image-wise exposure and a single development step.

30

Further advantages and embodiments of the present invention will become apparent from the following description.

35

DETAILED DESCRIPTION OF THE INVENTION

Before setting out the elements of the present invention, some terms of the appending claims will be defined. The term "support" is

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used in the meaning of a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support but which is not self-supporting.

The term "electroconductive" is related to the electric resistivity of the material. The electric resistivity of a layer is generally expressed in terms of volume resistivity R_s (unit Ω ; often specified as Ω/\square). Alternatively, the electroconductivity may be expressed in terms of surface resistivity $R_v = R_s \cdot d$, wherein d is the thickness of the layer, or in units of conductance $k_i = 1/R_i$ ($i=s,v$; unit=S(iemens)= $1/\Omega$). $10^5 \Omega/\square$ is typically regarded as a value of surface resistivity which distinguishes electroconductive materials from anti-static materials. So to term "electroconductive" as used herein is preferably interpreted as "having a surface resistivity below $10^5 \Omega/\square$ ". Anti-static materials typically have a surface resistivity in the range from 10^6 to $10^{11} \Omega/\square$ and cannot be used as an electrode.

All values of electric resistivity presented herein are measured according to the following method. The support coated with the electroconductive layer is cut to obtain a strip having a length of 27.5 cm and a width of 35 mm. Over the width of the strip electrodes are applied at a distance of 10 cm. The electrodes are made of a conductive polymer, ECCOCOAT CC-2 available from Emerson & Cumming Speciality polymers. Over said electrode a constant potential is applied and the current flowing through the circuit is measured on a Pico-amperemeter KEITHLEY 485. From the potential and the current, taking into account the geometry of the area between the electrodes, the surface resistivity in Ω/\square is calculated.

The solubility in a developer of the light- or heat-sensitive layer used in the present invention is capable of being differentiated upon exposure, i.e. the solubility can either be rendered more (positive working) or less (negative working) soluble in a developer upon exposure to light or heat. Said layer preferably comprises a positive or negative working photoresist as active ingredient, i.e. a compound or composition of which the solubility can be differentiated upon exposure. Suitable examples of such photoresists are given below. According to such preferred embodiment, the patterning method does not require a heat- or light-induced crosslinking of the electroconductive polymer itself.

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The positive working layer preferably comprises an o-naphthoquinonediazide compound (NQD) and an alkali soluble resin. Particularly preferred are o-naphthoquinonediazidosulphonic acid esters or o-naphthoquinone diazidocarboxylic acid esters of various hydroxyl compounds and o-naphthoquinonediazidosulphonic acid amides or o-naphthoquinone-diazidocarboxylic acid amides of various aromatic amine compounds.

Two variants of NQD systems can be used : one-component systems and two-component systems. In the former case, the sulphonic or carboxyl acid group is linked directly to the phenolic hydroxy group of a water insoluble, alkali soluble or swellable resins having a phenolic hydroxy group. It is preferred that some phenolic hydroxy groups remain unsubstituted. Examples of such compounds include phenol, cresol, resorcinol and pyrogallol. Examples of preferred water insoluble, alkali soluble or swellable resins having a phenolic hydroxy group include phenol-formaldehyde resin, cresol-formaldehyde resin, pyrogallol-acetone resin and resorcinol-benzaldehyde resin. Typical examples include esters naphthoquinone-(1,2)-diazidosulphonic acid and phenol-formaldehyde resin or cresol-formaldehyde resin, esters of naphthoquinone-(1,2)-diazido-(2)-5-sulphonic acid and pyrogallol-acetone resin as disclosed in U.S. Patent No. 3,635,709 and esters of naphthoquinone-(1,2)-diazido-(2)-5-sulphonic acid and resorcinol-pyrogallol-acetone copolycondensates as disclosed in J.P. KOKAI No. Sho 55-76346.

Examples of other useful compounds are polyesters having hydroxyl groups at their termini esterified with o-naphthoquinone-diazidesulphonyl chloride as disclosed in J.P. KOKAI No. Sho 50-117503; homopolymers of p-hydroxystyrene or copolymers thereof with other copolymerizable monomers esterified with o-naphthoquinone-diazidosulphonyl chloride as disclosed in J.P. KOKAI No. Sho 50-113305; condensates of alkyl acrylate-acryloyloxyalkyl carbonate - hydroxyalkyl acrylate copolymers with o-naphthoquinonediazido-sulphonyl chloride as disclosed in U.S. Patent No. 3,859,099; amides of copolymers of p-aminostyrene and monomers copolymerizable therewith and o-naphthoquinonediazido-sulphonic acid or o-naphthoquinonediazidocarboxylic acid as disclosed in U.S. Patent No. 3,759,711; as well as ester compounds of polyhydroxybenzophenone and o-naphthoquinonediazidosulphonyl chloride.

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These compounds may be used alone but are preferably used as a mixture with an alkali-soluble resin to form a light-sensitive layer.

In the application of NQD as two-component systems various low-molecular NQD sulphonic or carboxyl acid derivatives are dissolved mainly in certain water insoluble, alkali soluble or swellable resins; the latter acts as polymeric binder for NQD. Preferably said 4- or 5- sulphonyl or carboxyl substituted 1,2 naphthoquinone-diazides are esters of 1,2 naphthoquinonediazides-4- or -5-sulphonic or carboxylic acids with a phenolic compound having at least two phenolic hydroxy groups, more preferably with a phenolic compound having at least three phenolic hydroxy groups. Further suitable 1,2 naphthoquinone-2-diazides are disclosed in GB-A 739654 and in US-A 4,266,001.

Preferred water insoluble, alkali soluble or swellable resins are resins, which comprise phenolic hydroxy groups, oxime groups or sulphonamido groups. More preferred are resins having phenolic hydroxy groups, and phenolic hydroxy functionalized derivatives of poly(meth)acrylates, which can be synthesised starting from e.g. hydroxyethyl (meth)acrylate.

Most preferred are synthetic novolac resins and typical examples thereof are phenolformaldehyde resin, cresol-formaldehyde resin, and phenol-cresol-formaldehyde copolycondensed resins as disclosed in J.P. KOKAI No. Sho 55-57841

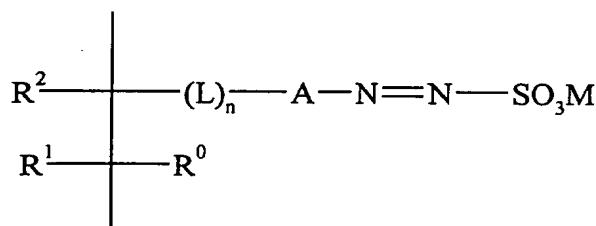
The negative working layer preferably comprises a diazonium salt, a diazonium resin or an aryldiazosulfonate homo- or copolymer. Examples of low-molecular weight diazonium salts for use in the present invention include: benzidine tetrazoniumchloride, 3,3'-dimethylbenzidine tetrazoniumchloride, 3,3'-dimethoxybenzidine tetrazoniumchloride, 4,4'-diaminodiphenylamine tetrazoniumchloride, 3,3'-diethylbenzidine tetrazoniumsulfate, 4-aminodiphenylamine diazoniumsulfate, 4-aminodiphenylamine diazoniumchloride, 4-piperidino aniline diazoniumsulfate, 4-diethylamino aniline diazoniumsulfate and oligomeric condensation products of diazodiphenylamine and formaldehyde. Examples of diazo resins useful in the present invention include condensation products of an aromatic diazonium salt as the light-sensitive substance. Such condensation products are described, for example, in DE-P-1 214 086.

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The light- or heat-sensitive layer preferably also contains a binder e.g. polyvinyl alcohol.

Upon exposure the diazo resins or diazonium salts are converted from water soluble to water insoluble (due to the destruction of the diazonium groups) and additionally the photolysis products of the diazo may increase the level of crosslinking of the polymeric binder or diazo resin, thereby selectively converting the surface, in an image pattern, from water soluble to water insoluble. The unexposed areas remain unchanged, i.e. water-soluble.

Other preferred examples of negative working compounds are aryldiazosulfonate homo- or copolymers which can be prepared by homo- or copolymerization of aryldiazosulfonate monomers with other aryldiazosulfonate monomers and/or with vinyl monomers such as (meth)acrylic acid or esters thereof, (meth)acrylamide, acrylonitrile, vinylacetate, vinylchloride, vinylidene chloride, styrene, alpha-methyl styrene etc. Suitable aryldiazosulfonate polymers for use in the present invention have the following formula:



wherein $R^{0,1,2}$ each independently represent hydrogen, an alkyl group, a nitrile or a halogen, e.g. Cl, L represents a divalent linking group, n represents 0 or 1, A represents an aryl group and M represents a cation.

L preferably represents divalent linking group selected from the group consisting of:

$-(X)_t-CONR^3-$, $-(X)_t-COO-$, $-X-$ and $-(X)_t-CO-$, wherein t represents 0 or 1, R^3 represents hydrogen, an alkyl group or an aryl group, X represents an alkylene group, an arylene group, an alkyleneoxy group, an arylenoxy group, an alkylenthio group, an arylenthio group, an alklenamino group, an arylamino group, oxygen, sulfur or an aminogroup.

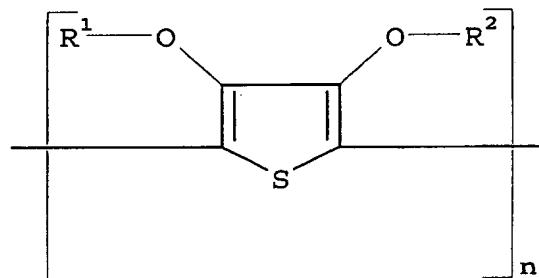
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A preferably represents an unsubstituted aryl group, e.g. an unsubstituted phenyl group or an aryl group, e.g. phenyl, substituted with one or more alkyl group, aryl group, alkoxy group, aryloxy group or amino group.

5 M preferably represents a cation such as NH_4^+ or a metal ion such as a cation of Al, Cu, Zn, an alkaline earth metal or alkali metal.

10 Specific examples of suitable aryldiazosulfonate polymers are described in EP-A-771 645. The weight ratio of the amount of the aryldiazosulfonate homo- or copolymer versus the amount of 10 electroconductive polymer is preferably between 10:200 to 400:200.

15 The electroconductive polymer used according to the present invention can be any intrinsically conductive polymer known in the art, e.g., polyacetylene, polypyrrole, polyaniline, polythiophene, etc. Preferably a polythiophene is used. The polythiophene used according to the method of this invention has preferably the following formula:



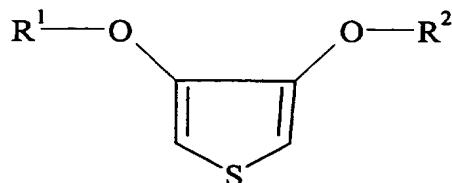
20 in which n is larger than 1 and each of R^1 and R^2 independently represents hydrogen or an optionally substituted C_{1-4} alkyl group or together represent an optionally substituted C_{1-4} alkylene group or an optionally substituted cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, an 25 optionally C_{1-12} alkyl- or phenyl-substituted ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.

The preparation of such a polythiophene and of aqueous dispersions containing such a polythiophene and a polyanion is described in EP-A-440 957 and corresponding US-P-5 300 575.

30 Basically the preparation of polythiophene proceeds in the presence

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of polymeric polyanion compounds by oxidative polymerisation of 3,4-dialkoxythiophenes or 3,4-alkylenedioxythiophenes according to the following formula:



wherein R¹ and R² are as defined above.

Stable aqueous polythiophene dispersions having a solids content of 0.05 to 55% by weight and preferably of 0.1 to 10% by weight can be obtained by dissolving thiophenes corresponding to the formula above, a polyacid and an oxidising agent in an organic solvent or preferably in water, optionally containing a certain amount of organic solvent, and then stirring the resulting solution or emulsion at 0°C to 100°C until the polymerisation reaction is completed. The polythiophenes formed by the oxidative polymerisation are positively charged, the location and number of such positive charges being not determinable with certainty and therefore not mentioned in the general formula of the repeating units of the polythiophene polymer.

The oxidising agents are those which are typically used for the oxidative polymerisation of pyrrole as described in for example J. Am. Soc. 85, 454 (1963). Preferred inexpensive and easy-to-handle oxidising agents are iron(III) salts, e.g. FeCl₃, Fe(ClO₄)₃ and the iron(III) salts of organic acids and inorganic acids containing organic residues. Other suitable oxidising agents are H₂O₂, K₂Cr₂O₇, alkali or ammonium persulfates, alkali perborates, potassium permanganate and copper salts such as copper tetrafluoroborate. Air or oxygen can also be used as oxidising agents. Theoretically, 2.25 equivalents of oxidising agent per mol of thiophene are required for the oxidative polymerisation thereof (J. Polym. Sci. Part A, Polymer Chemistry, Vol. 26, p.1287, 1988). In practice, however, the oxidising agent is used in excess, for example, in excess of 0.1 to 2 equivalents per mol of thiophene.

The polyacid forms a polyanion or, alternatively, the polyanion can be added as a salt of the corresponding polyacids, e.g. an

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alkali salt. Preferred polyacids or salts thereof are polymeric carbonic acids such as poly(acrylic acid), poly((meth)acrylic acid) and poly(maleic acid) or polymeric sulphonic acids such as poly(styrene sulphonic acid) or poly(vinyl sulphonic acid).

5 Alternatively, copolymers of such carbonic and/or sulphonic acids and of other polymerizable monomers such as styrene or acrylates can be used. Poly(styrene sulphonic acid) is especially preferred. The molecular weight of these polyanion forming polyacids is preferably between 1000 and 2×10^6 , more preferably between 2000 and 5×10^5 . These 10 polyacids or their alkali salts are commercially available and can be prepared according to the known methods, e.g. as described in Houben-Weyl, Methoden der Organische Chemie, Bd. E20 Makromolekulare Stoffe, Teil 2, (1987), pp. 1141.

15 Similar methods are known for the preparation of other electroconductive polymers such as polyacetylene, polypyrrole, and polyaniline. The electroconductive polymer dispersions thus obtained can then be used as basic ingredient of a coating solution. The coating solution can also comprise additional ingredients, such as one or more binders, one or more surfactants, spacing particles, UV-20 filters or IR-absorbers. Suitable polymer binders are described in EP-A 564 911. Such binders may be treated with a hardening agent, e.g. an epoxysilane as described in EP-A 564 911, which is especially suitable when coating on a glass substrate. In the embodiment according to the present invention wherein the 25 electroconductive polymer is contained in the heat- or light-sensitive layer, also the negative or positive working compounds discussed above are present in the same coating solution as the electroconductive polymer.

30 Especially when polythiophene is used as the electroconductive polymer, the coating solution preferably also comprises an organic compound that is:

- a linear, branched or cyclic aliphatic C₂₋₂₀ hydrocarbon or an optionally substituted aromatic C₆₋₁₄ hydrocarbon or a pyran or a furan, said organic compound comprising at least two hydroxy groups or at least one -COX or -CONYZ group wherein X denotes -OH and Y and Z independently of one another represent H or alkyl; or
- a heterocyclic compound containing at least one lactam group.

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Examples of such organic compounds are e.g. N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethyl-2-imidazolidone, N,N,N',N'-tetramethylurea, formamide, dimethylformamide, and N,N-dimethylacetamide. Preferred examples are sugar or sugar derivatives such as arabinose, saccharose, glucose, fructose and lactose, or di- or polyalcohols such as sorbitol, xylitol, mannitol, mannose, galactose, sorbose, gluconic acid, ethylene glycol, di- or tri(ethylene glycol), 1,1,1-trimethylol-propane, 1,3-propanediol, 1,5-pentanediol, 1,2,3-propanetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, or aromatic di- or polyalcohols such as resorcinol.

Suitable supports for use in the methods of the present invention are polymeric films such as poly(ethylene terephthalate), poly(ethylene naphthalate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefines, polyvinylchloride, etc. optionally provided with a subbing layer. Also inorganic substrates can be used such as silicon, ceramics, oxides, glass, polymeric film reinforced glass, glass/plastic laminates.

The material of the present invention can be image-wise exposed to ultraviolet light optionally in combination with blue light in the wavelength range of 250 to 500 nm. Upon image-wise exposure, a differentiation of the solubility in a developer of the exposed and non-exposed areas is induced. Useful exposure sources are high or medium pressure halogen mercury vapour lamps, e.g. of 1000 W. When the image recording layer comprises a heat-sensitive compound such as the aryldiazosulfonates discussed above, the material may also be exposed by infrared light, e.g. by a laser having an emission wavelength in the range from about 700 to about 1500 nm, such as a semiconductor laser diode, a Nd:YAG or a Nd:YLF laser. In the latter embodiment, IR-absorbing compounds such as IR-sensitive dyes or pigments are preferably added to the image recording layer. Highly preferred are IR sensitive dyes or pigments which do not substantially absorb visible light as disclosed in WO-A-95 7822.

After the image-wise exposure the material is developed in a developer which can be plain water or is preferably water-based. During development the exposed (positive working) or non-exposed (negative working) areas together with the electroconductive polymer are removed and an electroconductive pattern is thereby obtained.

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Suitable aqueous developers are water, AZ303 (Clariant) or EN232 (Agfa). When a subbing layer (also called substrate layer) is present on the support the material is preferably rubbed thoroughly with a tissue during development to avoid remnant conductivity. Said rubbing can be done in the processing fluid or in a separate water bath after the development stage. Equal results can be obtained by applying a high pressure water jet after the development stage, in this way avoiding contacting the conductive areas.

In a highly preferred embodiment of the present invention the support comprises no subbing layer but, instead, has been treated with a corona discharge. Such materials can be developed while softly rubbing and still yield an excellent conductivity ratio between exposed and non-exposed areas.

15 Examples

While the present invention will hereinafter be described in connection with preferred embodiments thereof, it will be understood that it is not intended to limit the invention to those embodiments.

20 The dispersions of poly(3,4-ethylenedioxy-thiophene) / polystyrene sulfonate complex as used hereinafter were prepared according to the method described in EP-A-99202705 filed on 23.08.1999.

25 Example 1

In the present example, a negative working light-sensitive compound was used as a photoresist for patterning a polythiophene 30 layer. A substrated polyethylene terephthalate film support was coated with 40ml/m² of the following coating solution (table 1) (40µm wet thickness).

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Table 1: composition of the coating solutions (in ml)

| solution/ingredient | Sample | | | | | | |
|--|--------|-----|-----|-----|-----|-----|-----|
| | I (*) | II | III | IV | V | VI | VII |
| 1.2% aqueous dispersion of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulfonate complex | 417 | 417 | 417 | 417 | 417 | 417 | 417 |
| 0.25% aqueous solution of diphenylamine diazonium resin (Negalux N18 from PCAS) | / | 100 | 250 | 500 | | | |
| 0.25% aqueous solution of diazo resin No.8 (Fairmount Chemical) | / | / | / | / | 100 | 250 | 500 |
| 30% aqueous solution of a copolymer (vinylidene chloride, methylmethacrylate, itaconic acid (88/10/2)) | 8.3 | / | / | / | / | / | / |
| 2% aqueous solution of a spreading agent | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| N-methyl pyrrolidone | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| Water | 514.7 | 423 | 273 | 23 | 423 | 423 | 423 |

(*) comparison

5

After drying, all the above samples comprised 200 mg/m² of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate complex. The samples were exposed through a mask on a PRINTON™ CDL 1502i UV contact exposure unit (from Agfa) and processed with plain water. The results are presented in table 2.

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Table 2

| property | Sample | | | | | | |
|--|--------|-----|-----|-----|-----|-----|------|
| | I (*) | II | III | IV | V | VI | VII |
| Differentiation after processing between exposed and non-exposed areas | no | yes | yes | yes | yes | yes | yes |
| Resistance (ohm/square) of coated layer before patterning | 730 | 760 | 650 | 980 | 490 | 620 | 1500 |
| Resistance (ohm/square) of the exposed areas after exposure and processing | 730 | 850 | 650 | 960 | 480 | 630 | 1500 |

(*) comparison

5 The results in table 2 show that for the samples II to VII according to the invention structured conducting poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layers were obtained and that the patterning method of exposure and developing does not substantially affect the conductivity of the layer. The surface 10 resistivity of the non-exposed areas was above $10^4 \Omega/\square$. A surface resistivity in the non-exposed areas above $10^{10} \Omega/\square$ could be obtained when the material was rubbed thoroughly with a tissue during processing.

15 Example 2

20 In the present example, a negative working light-sensitive compound was used as a photoresist for patterning a polythiophene layer. A substrated polyethylene terephthalate film support was coated with 40ml/m² of the following coating solution (table 3) (40µm wet thickness).

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Table 3: composition of the coating solutions (in ml)

| solution/ingredient | Sample | | | | | | |
|---|---------|-----|-----|-----|------|------|------|
| | VIII(*) | IX | X | XI | XII | XIII | XIV |
| 1.2% aqueous dispersion of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate complex | 417 | 417 | 417 | 417 | 417 | 417 | 417 |
| 17% solution in isopropylalcohol/water (60/40) of the copolymer (methylmethacrylate, sodium-4-methacryloyl-aminophenyldiazosulfonaat (82/18)) | / | 1.5 | 3.7 | 7.1 | 14.2 | 28.4 | 56.8 |
| 30% aqueous solution of the copolymer (vinylidene chloride, methyl-methacrylate, itaconic acid (88/10/2)) | 8.3 | / | / | / | / | / | / |
| 2% aqueous solution of a spreading agent | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| N-methyl pyrrolidone | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| water | 514.7 | 522 | 519 | 516 | 509 | 495 | 466 |

(*) comparison

5 After drying, all the above samples VIII-XIV comprised 200 mg/m² of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate complex. The samples were exposed through a mask on a PRINTON™ CDL 1502i UV contact exposure unit (from Agfa) and processed in water while rubbing with a tissue under water. The results are presented
10 in table 4

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Table 4

| property | Sample | | | | | | |
|--|---------|------|------|------|------|------|-------|
| | VIII(*) | IX | X | XI | XII | XIII | XIV |
| Differentiation after processing between the exposed and the non-exposed areas | no | yes | yes | Yes | yes | yes | yes |
| Resistance (ohm/square) of coated layer before patterning | 760 | 689 | 739 | 790 | 1100 | 1600 | 5500 |
| Resistance (ohm/square) of exposed areas after exposure and processing | 760 | 1344 | 1375 | 1360 | 2100 | 2400 | 22000 |

(*) comparison

5 The results from table 4 show that in the samples IX to XIV according to the invention structured conducting poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layers were obtained. The surface resistivity of the non-exposed areas was above $10^5 \Omega/\square$. A surface resistivity in the non-exposed areas above $10^{10} \Omega/\square$ could be obtained when the material was rubbed thoroughly with a tissue during processing.

Example 3

15 In the present example, a negative working light-sensitive compound was used as a photoresist for patterning a polythiophene layer. A substrated polyethylene terephthalate film support (sample XV, XVI, XVII) and an unsubbed corona treated polyethylene terephthalate film support (sample XVIII) were coated with $40\text{ml}/\text{m}^2$ 20 of the following coating solution (table 5) ($40\mu\text{m}$ wet thickness).

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Table 5: composition of the coating solutions (in ml)

| Solution/ingredient | sample | | | |
|---|--------|-----|------|-------|
| | XV | XVI | XVII | XVIII |
| 1.2% aqueous dispersion of poly(3,4-ethylenedioxy-thiophene) / polystyrene sulphonate complex | 417 | 417 | 417 | 417 |
| 17,8% aqueous solution of the homopolymer of sodium-4-methacryloyl-aminophenyl diazosulfonaat | 7 | 14 | 21 | 14 |
| 2% aqueous solution of a spreading agent | 10 | 10 | 10 | 10 |
| N-methyl pyrrolidone | 50 | 50 | 50 | 50 |
| water | 516 | 509 | 502 | 509 |

After drying, all the above samples XV-XVIII comprised 200 mg/m² of poly(3,4-ethylenedioxy-thiophene) / polystyrene sulphonate complex. The sample was exposed through a mask on a PRINTON™ CDL 1502i UV contact exposure unit (from Agfa) and processed in water (softly rubbing with a tissue under water). The results are presented in table 6.

Table 6

| property | Sample | | | |
|--|---------------------|----------------------|---------------------|----------------------|
| | XV | XVI | XVII | XVIII |
| Differentiation after processing between the exposed and the non-exposed areas | Yes | Yes | Yes | Yes |
| Resistance (ohm/square) of coated layer before patterning | 1.7x10 ³ | 5.2x10 ³ | 1.5x10 ⁴ | 3.8x10 ³ |
| Resistance (ohm/square) of the exposed areas after exposure and processing | 4.8x10 ⁴ | 1.6 x10 ⁴ | 1.5x10 ⁵ | 1.2x10 ⁴ |
| Resistance (ohm/square) of the non-exposed areas after exposure and processing | 2.4x10 ⁵ | 4.2x10 ⁵ | 6.3x10 ⁵ | 3.5x10 ¹¹ |
| Resistance ratio non-exposed / exposed areas | 5 | 26 | 4 | >10 ⁷ |

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The results in Table 6 indicate that the resistance ratio is low when samples XV, XVI and XVII, which contain a subbing layer on the support, are processed by rubbing the material softly in water. A much higher contrast ratio can be obtained by either using a support which does not contain a substrate but instead has been treated with a corona discharge (sample XVIII, last column of Table 6) or by rubbing thoroughly with a tissue during processing (results not shown in Table 6).

The mask used for exposing the above samples consisted of alternating lines of high and low density, the lines having a width of 6 μm . These lines were reproduced very well in the patterned material, which showed conducting lines and non-conducting spaces of similar width.

15

Example 4

Samples VIII, IX, X, XI and XII of example 2 were image-wise exposed in heat-mode with a NdYAG laser (1064 nm) having a spot size of 22 μm , a pitch of 11 μm and a scan speed of 2m/s. The image plane power was set at 100mW. The exposed samples were processed in water (softly rubbing with a tissue under water).

For the samples IX, X, XI and XII structured poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layers were obtained having a similar surface resistivity as in Example 2. For sample VIII (comparison) no structured conducting poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layer was obtained, since the poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layer was removed in the non-exposed as well as in the exposed areas. The surface resistivity of the non-exposed areas was above $10^4 \Omega/\square$. A surface resistivity in the non-exposed areas above $10^{10} \Omega/\square$ could be obtained when the material was rubbed thoroughly with a tissue during processing.

35 Example 5

Samples VIII, IX, X, XI and XII of example 2 were image-wise exposed in heat-mode with a diode laser (830nm) having a spot size

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of $11\mu\text{m}$, a pitch of $6\mu\text{m}$ and a scan speed of 2m/s . The image plane power was set at 81mW . The exposed samples were processed in water (softly rubbing with a tissue under water). The results were similar to those obtained in Example 4.

5

Example 6

10 In the present example, a positive working light-sensitive photoresist was used for patterning a polythiophene layer.

15 A substrated polyethylene terephthalate film support was first coated with a solution of AZ7217 (positive working photoresist from Clariant) in methyl-ethylketone (1:3 v:v) ($15\mu\text{m}$ wet thickness). On top of this layer the following coating solution (table 7) was applied ($67\mu\text{m}$ wet thickness):

Table 7: composition of the coating solutions (in ml)

| solution/ingredient | sample | |
|--|--------|-----|
| | XIX | XX |
| 1.2% aqueous dispersion of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulfonate complex | 125 | 125 |
| Z6040 (from Dow Corning) | 1.0 | 1.0 |
| 2% aqueous solution of a spreading agent | 1.5 | 1.5 |
| N-methyl pyrrolidone | 50 | 50 |
| Water | 825 | 450 |

20

After drying, the above samples XIX and XX comprised 200 mg/m^2 of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulfonate complex. The samples were exposed from the support side through a mask on a PRINTON CDL 1502i UV contact exposure unit and processed with AZ303 (Clariant).

Image-wise structured conducting poly(3,4-ethylenedioxy-thiophene)/polystyrene sulfonate layers were obtained. The

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5 patterning method of exposure and developing does not effect the conductivity of the layer. The surface resistivity of the non-exposed areas was typically of the order of $10^4 \Omega/\square$. A surface resistivity in the exposed areas above $10^{10} \Omega/\square$ could be obtained when the material was rubbed thoroughly with a tissue during processing.

Example 7

10 In the present example, a positive photoresist and the electroconductive polymer were present in the same layer. A substrated polyethylene terephthalate film support was coated with 50ml/m² of the following coating solution (table 8) (50µm wet thickness).

15

Table 8: composition of the coating solutions (in ml)

| solution/ingredient | sample |
|--|--------|
| | XXI |
| 1.2% aqueous dispersion of poly(3,4-ethylenedioxy-thiophene)/polystyrene sulfonate complex | 300 |
| AZ 7217 (positive working photoresist from Clariant) | 100 |
| 2% aqueous solution of a spreading agent | 40 |
| N-methyl pyrrolidone | 560 |

20 The samples were exposed through a mask on a PRINTON CDL 1502i UV contact exposure unit and processed with AZ351B (Clariant). Image-wise structured conducting poly(3,4-ethylenedioxy-thiophene)/polystyrene sulphonate layers were obtained. The surface resistivity of the non-exposed areas was typically $5 \cdot 10^3 \Omega/\square$. A surface resistivity in the exposed areas above $10^{10} \Omega/\square$ could be obtained when the material was rubbed thoroughly with a tissue.



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[CLAIMS]

1. Material for making an electroconductive pattern, the material comprising a support and a light- or heat-sensitive layer of which the solubility in a developer is capable of being differentiated upon exposure, characterised in that the light- or heat-sensitive layer further contains an electroconductive polymer.

5

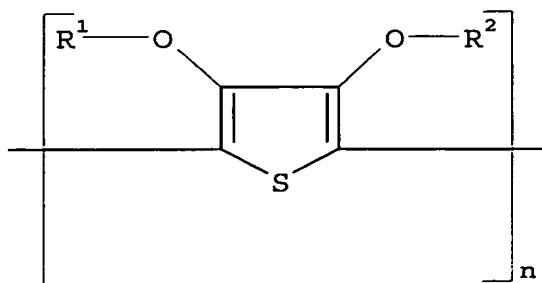
2. Material for making an electroconductive pattern, the material comprising in the order given a support, a light- or heat-sensitive layer of which the solubility in a developer is capable of being differentiated upon exposure, and a layer comprising an electroconductive polymer.

10

3. Material according to claim 1 or 2 wherein the electroconductive polymer layer comprises a polythiophene and a polyanion.

15

4. Material according to claim 3, wherein the polythiophene corresponds to the following formula :



20

in which n is larger than 1 and each of R¹ and R² independently represent hydrogen or an optionally substituted C₁₋₄ alkyl group or together represent an optionally substituted C₁₋₄ alkylene group or an optionally substituted cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, an optionally C₁₋₁₂ alkyl- or phenyl-substituted ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.

25

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5. Material according to any of the preceding claims wherein the polyanion is a poly(styrene sulphonate).
6. Material according to any of the preceding claims wherein the layer comprising the electroconductive polymer has a surface resistivity lower than $10^5 \Omega/\square$.
7. Material according to any of the preceding claims wherein the light- or heat-sensitive layer is a negative working layer comprising a diazonium salt or resin.
8. Material according to any of the preceding claims wherein the light- or heat-sensitive layer is a negative working layer comprising an aryldiazosulfonate homo- or copolymer.
9. Material according to claim 8 wherein the weight ratio of the amount of aryldiazosulfonate homo- or copolymer versus the amount of electroconductive polymer is between 10:200 to 400:200.
10. Material according to any of the preceding claims wherein the light- or heat-sensitive layer is a positive working layer comprising a quinonediazide compound.
11. Material according to any of the preceding claims wherein the support is treated with a corona discharge.
20. 12. Method of making an electroconductive pattern on a support comprising the steps of
 - providing a material according to any of the preceding claims;
 - image-wise exposing the material thereby obtaining a differentiation of the solubility in a developer of the exposed and the non-exposed areas of the light- or heat-sensitive layer;
 - processing the material with the developer, thereby removing soluble areas of the light- or heat-sensitive layer.
25. 13. Method of making an electroconductive pattern on a support comprising the steps of

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- providing a material according to any of claims 2 to 11;
- image-wise exposing the material thereby obtaining a differentiation of the solubility in a developer of the exposed and the non-exposed areas of the light- or heat-sensitive layer;
- processing the material with the developer, thereby simultaneously removing soluble areas of the light- or heat-sensitive layer as well as overlying areas of the layer comprising the electroconductive polymer.

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[ABSTRACT]

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Material and method for making an electroconductive pattern

5 A material for making an electroconductive pattern is disclosed, the material comprising a support and a light- or heat-sensitive layer containing an electroconductive polymer. Alternatively, the material comprises in the order given a support, a light- or heat-sensitive layer and a layer comprising an 10 electroconductive polymer. The solubility of the light- or heat-sensitive layer in a developer can be differentiated by image-wise exposure. These materials can be patterned by a simple, convenient method that involves a low number of steps and that does not require the use of hazardous chemicals.

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